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Raman Spectroscopy of Multi-Layer Graphene epitaxially Grown on 4H-SiC by Joule Heat Decomposition

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Abstract

We developed a Joule heating decomposition (JHD) method, which applied direct current on the SiC for the epitaxial growth of multi-layer graphene (MLG) films on Si-terminated (0001) face of the high doping 4H-SiC substrate. By this JHD method, the growth time for preparing MLG was only several minutes. Raman spectroscopy was employed to study the influence of the temperature caused by the Joule heating on the quality and the uniformity of the sample. Then, other properties, such as the strain, the layer's number, and the electric characteristics, of the MLG were studied in details. It was found that the quality of the MLG was substantially dependent on the growth temperature (operation current) and the growth time, while the layer's number was only dependent on the growth temperature but not the growth time. Finally, less-defect and homogeneous MLG (~ 45 layers) with an area of ~ 12×5 mm^2 could be obtained at a heating temperature of ~ 1470 °C with duration time of 5 min. By using the linear transmission line method, the specific contact resistance of Au and MLG was 5.03×10^{-5} Ω cm^2, and the sheet resistance was 52.36 Ω/sq, respectively.

Keywords: Carbon materials, Semiconductors, Raman

Background

Graphene, as a monolayer of carbon (C) atoms with two-dimentional honeycomb lattice, has triggered extensive investigations due to its remarkable mechanical, electronic, and thermal properties in the past decade [1, 2]. Its mechanical and photoelectronic characteristics make it an ideal material for the nanoelectronics, thin-film transistors, transparent electrodes, and printable photoelectronics [3, 4]. Up to today, several techniques for synthesizing large-scale and high-quality graphene have been researched. Mechanical cleavage of graphene from highly oriented pyrolytic graphite produces high-quality but small-sized graphene monolayers [5]. Chemical vapor deposition (CVD) of hydrocarbons is used for epitaxial growth of large-area graphene on the surfaces of transition metals, such as Ni or Cu [6, 7]. Recently, Li and co-workers developed a method to grow graphene flakes directly on silicon with metal free by CVD method,

but the size of graphene was still very small [8]. Thermal decomposition of silicon carbide (SiC), by which silicon (Si) atoms are sublimated and a C-rich surface is retained to nucleate an epitaxial graphene (EG) layer, seems to be the promising method for EG production in large area, good quality, and high efficiency [9]. The main advantage of this method is that graphene can be epitaxially grown on the surface of SiC and directly applied to SiC-based optoelectronic and electronic devices without being transferred [10, 11], which could avoid the defects or damages caused during the transfer process of the graphene prepared by the methods of cleavage or CVD.

Recently, several thermal decomposition methods for EG growth have been reported, such as radio-frequency induction heating [12], laser heating [13], and other heating methods [14]. Comparing to these methods, we developed a Joule heating decomposition (JHD) method by applying direct current (DC) on SiC to generate Joule heating on the surface of SiC. By adjusting the DC, heating temperature on the surface of SiC could be modulated from ~ 1230 to 1600 °C or higher. The main advantages of JHD method over other thermal decomposition methods for preparing

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EG are that the temperature for growing EG on the surface of SiC could be reached in a few seconds and the size of the graphene layer could be produced as large as the size of SiC substrate which was prepared with an appropriate ratio of length and width. Therefore, the JHD method could be regarded as the low-cost and high efficiency method for EG growth on SiC. In this paper, Raman spectra of multi-layer graphene (MLG) epitaxially grown on 4H-SiC by JHD were studied to understand the influences of the operation current, growth temperature, and growth time on the structural and electrical properties of the MLG.

Methods/Experimental

Growth of Graphene on 4H-SiC

Two-inch N-type 4H-SiC (350 μm thick, ~ 0.02 Ω cm) wafers were purchased from SICC Materials Co., Ltd. A custom-made vacuum chamber and a ceramic cube with two aluminum (Al) and four small molybdenum (Mo) electrodes as a heating platform were used for the graphene growth. The wafers were sliced to several pieces of 25 mm × 5 mm substrates by a cutting machine before carefully treated by sonication with methanol, acetone, and ethanol three times, followed by wet-chemical RCA cleaning. After dried with N_2 flow, put the SiC substrate between

Mo electrodes on the heating platform, which was connected to a DC source, as shown in Fig. 1a. Subsequently, the base was placed into the vacuum chamber in which the air pressure will be vacuumed to ~ 10^{-6} Torr, followed by applying a DC on the SiC to generate a large Joule heat. With the DC applied from 2.79 to 3.43 A, the surface temperature of the SiC could be increased highly enough for the growth of graphene. After graphene growth, the samples were cooled down in the vacuum chamber for more than 4 h before characterization.

Sample Characterization

SiC substrates were cut by an automatic grinding wheel cutting machine, ZSH-406. The temperatures of sample's surface were measured by the MI16MB18 infrared thermometer from Sensortherm. Raman spectroscopy was carried out by WITec alpha 300RA confocal microscope system comprising of a laser with 488 nm wavelength and a UHTS 300 spectrograph (600 lines/mm grating, 30 cm focal length) coupled with a Peltier-cooled CCD detector. An atomic force microscope (AFM) (SPA-400) was used to characterize the morphology of the MLG before and after etching. The etching of MLG was performed by the inductively coupled plasma (ICP) 98 A with 30 sccm of
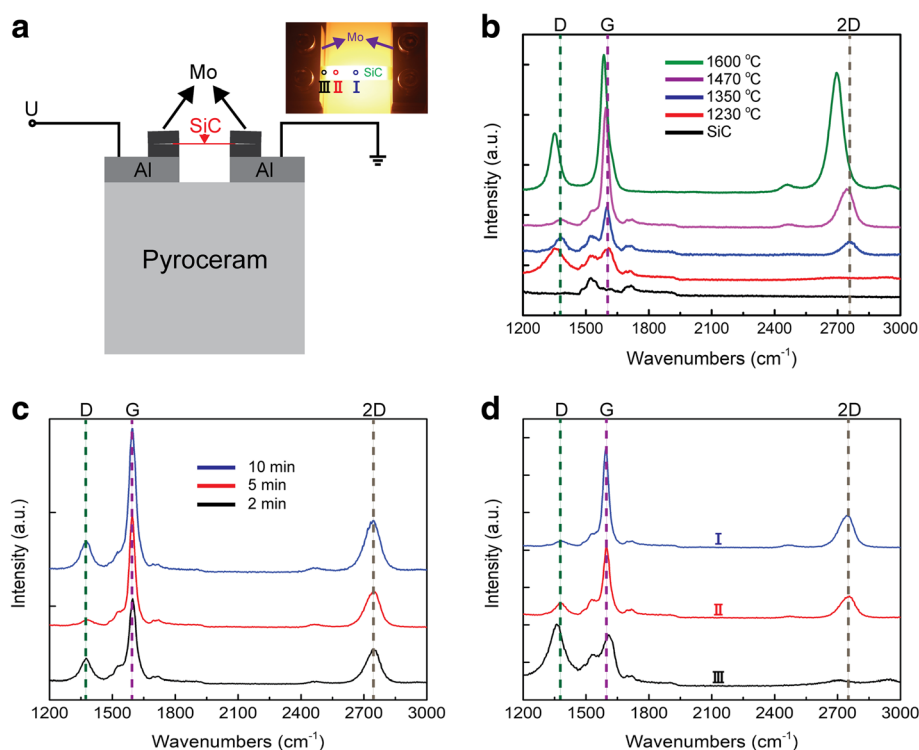

Fig. 1 a Schematic diagram of the platform for MLG growth by JHD. The inset was the image of the SiC during heating process. **b** Raman spectra of SiC and MLG grown on 4H-SiC (0001) at different growth temperatures for 5 min. **c** Raman spectra of MLG grown on 4H-SiC (0001) at 1470 °C for 2, 5, and 10 min, respectively. **d** Raman spectra characterized from the circled spots A, B, and C marked in the inset of **a** on the same sample. The sample was prepared at 3.24 A for 5 min

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O$_2$ for 60 s. The Au was deposited onto the MLG by evaporation using the same system as the growth process. A Au wire was heated to evaporate slowly by applying a DC on it, which was fixed on top of the MLG sample. With lithography, we prepared Au-graphene contact and measured the IV properties by the linear transmission line method (LTLM). The IV was carried out by using a Keithley 2410 SourceMeter and a Keithley 6514 system electrometer at room temperature.

Results and Discussion

Four MLG samples were prepared by applying different DCs of 2.79, 3.05, 3.24, and 3.43 A on the SiC substrates, and the DCs were kept stable for 5 min during the synthesis of graphene. With the increase of the DCs, the temperatures at the center of substrates were ~ 1230, 1350, 1470, and 1600 °C, respectively. After the growth of MLG was completed, the samples were investigated by Raman spectroscopy. As shown in Fig. 1b, several peaks corresponding to graphene were observed, which were identified by three main bands: (i) the defect-induced D band at frequency of ~ 1370 cm^{-1}, (ii) the in-plane vibrational G band at frequency of ~ 1600 cm^{-1}, and (iii) the two-phonon 2D band at frequency of ~ 2750 cm^{-1} [15]. Compared to a single-layer micromechanical cleavage graphene (MCG), an important observation was that the G (~ 1600 cm^{-1}) and 2D (~ 2750 cm^{-1}) bands of MLG shift significantly toward higher frequency from those of G (1580 cm^{-1}) and 2D (2673 cm^{-1}) of MCG [16]. There might be several reasons that caused the significant shifts of G band (~ 20 cm^{-1}) and 2D band (~ 77 cm^{-1}). Ni illustrated how the strain effect of the epitaxial graphene on 6H-SiC changed the lattice constant of graphene, and further affected the Raman frequencies [16]. Others have reported that the doping might cause the blue-shift of G and 2D peaks [17–19], but the effect was very weak comparing to the one aforementioned. Here, the blue-shift of G and 2D bands could be attributed to the strain effect which was caused by the lattice mismatch of graphene and SiC substrate [16]. From Fig. 1b, we observed the appearance of corresponding G band and D band of graphene from the red spectrum, which was taken from the MLG sample prepared at ~ 1230 °C. The high value of I_D (intensity of D band) divided by I_G (intensity of G band) (I_D/I_G) and no obvious evidence for 2D band indicated lots of defects and a poor crystallinity of graphene. The reason might be that C atoms could not obtain enough kinetic energy to process the reconstruction of the graphene well at such low growth temperature [20]. By increasing the heating temperature to ~ 1350 °C, the value of I_D/I_G decreased from ~ 1.01 to ~ 0.38, which indicated the MLG had a lower ratio of defects. The symmetric 2D band with a full width at half maximum (FWHM) ~ 72 cm^{-1} further demonstrated the crystallization of MLG

and its better quality. And, the low Raman intensity of SiC has proved that the samples we have prepared were the multi-layer graphene [21]. With the growth temperature further increased to 1470 °C, the I_D/I_G continued to decrease to ~ 0.06, indicating the number of defects was further reduced. Moreover, the 2D band had a slight red shift. We assume there might be a strain relief in the interface between MLG and SiC as more graphene layers formed at higher Joule heating temperature [16]. We also investigated the MLG that was prepared at ~ 1600 °C with Raman spectroscopy. However, a higher I_D/I_G (~ 0.43) was observed, indicating an increase of defects. Our hypothesis was that it might originate from the high graphitization rates in the out of equilibrium vacuum sublimation process, and thus, it caused more surface dislocations or corrugations on the surface of MLG [14]. Besides, further red shifts of D, G, and 2D bands were observed, which meant more strain relief, and thus, more graphene layers were synthesized [16].

We then focused on the influence of JHD process time on the growth of MLG. As the I_D/I_G of the MLG grown at 1470 °C was lowest, three samples were prepared at the DC of 3.24 A (~ 1470 °C) for 2, 5, and 10 min, respectively, and Raman spectra were shown in Fig. 1c. The I_D/I_G of the MLG grown for 5 min was about 0.06, which was lower than the other grown for 2 min (~ 0.41) and 10 min (~ 0.29), indicating that MLG grown for 5 min had the fewest defects. The reason might be that 2 min was too short for C atoms to reconstruct homogeneous graphene layers, and graphene defects such as discontinuity, inhomogeneity, and stacking disorder occasionally appeared. However, 10 min might be too long for MLG growth, as they would be affected by the residual gases in the chamber and thus generate defects [22]. As time increased, no red shift of G or 2D peak position was observed from Fig. 1c, indicating the strain between graphene layers and the substrate should be almost the same for these samples. The unchanged strain might be that the number of graphene layers was barely increased, as the I_G/I_{2D} were almost the same (2.7 for 2 min, 3.0 for 5 min, and 2.8 for 10 min) and the I_{SiC}/I_G was barely change, where I_{SiC} is the intensity of Raman band (at ~ 1520 cm^{-1}) for 4H-SiC [21].

Due to the thermal conductivity difference, the Joule heating power at the contact surface of SiC and Mo electrodes would escape faster. In that case, the substrate's center would obtain the highest temperature during the JHD process, while if the spot was closer to the Mo electrodes, the heating temperature would be lower. Therefore, Raman spectroscopy was used to characterize the MLG from different spots (as shown in the inset of Fig. 1a) on the sample prepared at the DC of 3.24 A, and the results were shown in Fig. 1d. The distances are about 3 mm between position C and

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B, and about 6 mm between positions B and A. Raman spectra of A and B showed rather a low value of I_D/I_G, along with symmetric 2D bands, which indicated few defects. The barely change of I_G/I_{2D} and I_{SiC}/I_G also proved similar layer's number of MLG between these two positions. Furthermore, no clear Raman shifts of the G and 2D band also demonstrated the homogeneity of MLG. Therefore, we could synthesize an area of ~ 12×5 mm^2 MLG with good uniformity of graphene layers by the JHD method.

To further study the uniformity of the MLG, Fig. 2a illustrated the optical image of the sample characterized from the area A in the inset of Fig. 1a. It is shown in Fig. 2a that most of the color contrast of the surface was quite even except for some dark dots. We found these dark dots had the highest intensity of 2D band, as shown in the Raman mapping of Fig. 2b. Figure 2c demonstrated the Raman spectra of the corresponding area marked in circles in Fig. 2b with a different color. It also showed that the intensity of G and 2D bands from the dark dots (black circle) were much higher than the other area. Besides, the peak position of both G and 2D bands was slightly red shifted. The hypothesis was that the formation of

graphene would prefer sites of screw dislocations or other defects (the dark dots in our work) on the surface of SiC [23], and the speed of decomposition of SiC, as well as the growth of graphene, would be faster than the other area. Figure 2d demonstrated the full width at half maximum (FWHM) of 2D band, which was rather uniform except for regions where defects of SiC were present.

To investigate the number of layers of the graphene that we prepared at ~ 1470 °C for 5 min, we use AFM to characterize the MLG sample after the ICP-etching, as shown in Fig. 3a. Etched with O$_2$, there was a terrace between MLG and the etched part. The inset in Fig. 3a also demonstrated the difference of contrast, while the light part was unetched and the dark part was etched. And the height profiles of the terrace at different positions on the AFM image were illustrated on Fig. 3b. To further confirm the existence of graphene after etching, Raman spectra were taken at the spots with and without ICP-etching, as shown in Fig. 3c. The unobvious D, G, or 2D bands proved that the graphene had been etched away completely. We then measured the average height difference between the MLG and the etched part thought the height profiles, and the value was ~
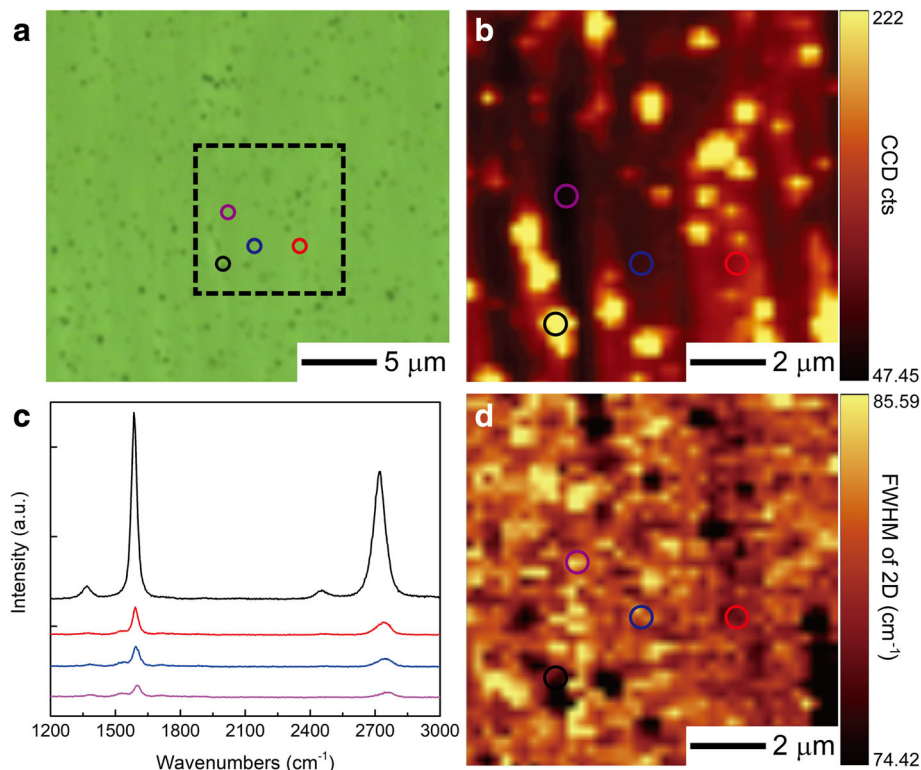

Fig. 2 a Optical image of MLG sample which was prepared at 3.24 A for 5 min and characterized from the center. **b** Raman mapping for the intensity of 2D band from the marked area in dashed square in **a**. **c** The Raman spectra from the marked circles in **b**. **d** Raman mapping for the FWHM of 2D band
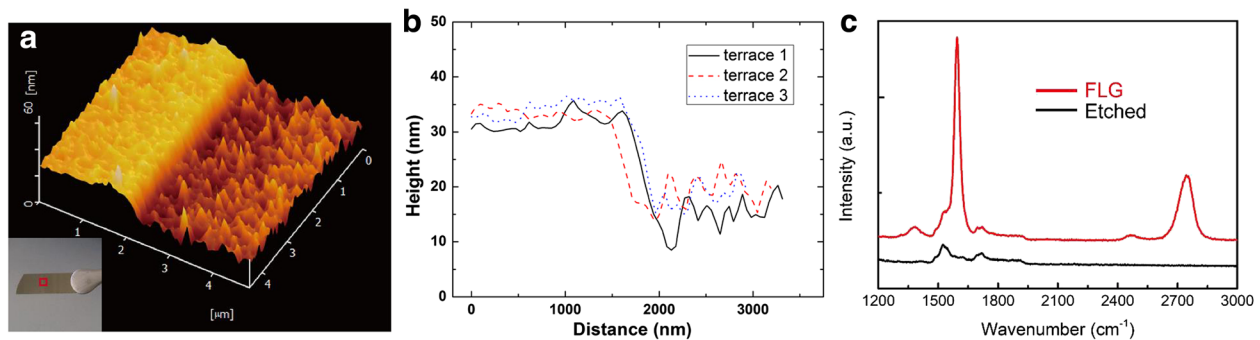
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Fig. 3 a AFM image of MLG with half etched by ICP-etching which was taken in the red square of the inset. The inset was the image of the MLG sample, and the light part was covered by MLG. The MLG was synthesized at 1470 °C for 5 min. **b** height profiles of the terrace at different position on the AFM image. The average height of the terrace is ~ 15.46 nm. **c** Raman spectra of the sample in **a**, the red and black spectra were corresponding to the sample before and after etching

15.46 nm, which meant the number of graphene layers was ~ 45 (the interlayer spacing was ~ 0.34 nm) [24]. Besides, the root-mean-square (RMS) value increased from 0.84 to 2.79 nm after ICP-etching, which might be due to the difference of decomposition speed of SiC caused by the defects and thus generate a rough surface of SiC after growth of graphene.

We then investigated the electric properties of the MLG (synthesized at ~ 1470 °C for 5 min). At room temperature, we measured the IV properties of the adjacent Au electrodes of the LTLM, as shown in Fig. 4a. According to the equations [25],

$$R_T = (\rho_s/Z)d + 2R_C \approx (\rho_s/Z)(d + 2L_T) \qquad (1)$$

$$\rho_c = \rho_s L_T^2 \qquad (2)$$

While R_T is the total resistance, ρ_s is the sheet resistance, R_C is the contact resistance, ρ_c is the specific contact resistance, Z is the width of the MLG (40 μm), d is the space between the Au electrodes (5, 10, 15, and 20 μm, respectively), and L_T is the length of transmission line for electricity. By the linear fit of the experimental data, as shown in Fig. 4b, we could get R_C and L_T. According to the Eqs. (1) and (2), ρ_s and ρ_c were calculated to be 52.36 Ω/sq and 5.03×10^{-5} Ω cm², respectively.

Conclusions

In summary, a convenient JHD method by applying DC power on SiC in vacuum (~ 10^{-6} Torr) was developed to grow multi-layer epitaxial graphene directly on 4H-SiC (0001) substrate. By optimizing the growth conditions, large-area (12 mm × 5 mm) and low-defect MLG with a good homogeneity could be obtained by heating SiC at ~ 1470 °C for 5 min, as Raman spectroscopy showed the lowest I_D/I_G. AFM result illustrated that the MLG was ~ 45 layers thick. The MLG also demonstrated a good
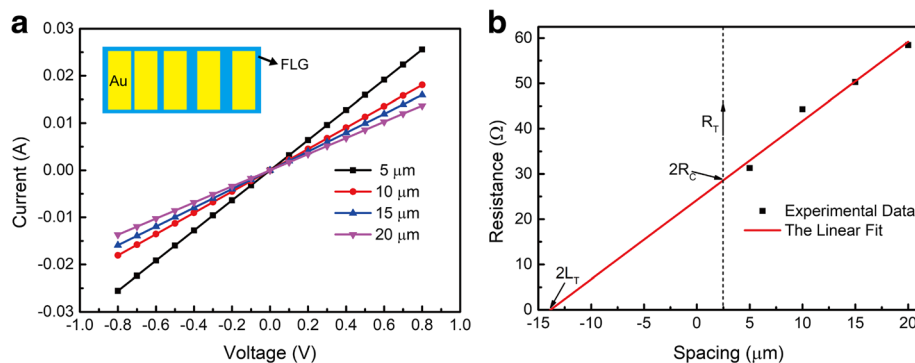

Fig. 4 a The IV properties of the Au-graphene-Au contact. The inset is the schematic diagram of LTLM. **b** The linear fit of the total contact resistance of Au ohmic contact as a function of contact pads distance from 5 to 20 μm

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ohmic contact with Au electrode. In our further works, epitaxial SiC on the SiC substrate will be selected for the MLG growth by JHD. Also, the low defect of SiC epitaxial layer would be another advantage for preparing MLG with high homogeneity and quality. Besides, the confinement control method such as introducing an inert gas will be employed into the JHD growth to adjust the growth rate, improve the quality, and obtain a higher homogeneity. The graphene produced by JHD method could be promising in the applications of SiC-based photoelectronic devices in the future.

Abbreviations

AFM: Atomic force microscope; Al: Aluminum; C: Carbon; CVD: Chemical vapor deposition; DC: Direct current; EG: Epitaxial graphene; FWHM: Full width at half maximum; ICP: Inductively coupled plasma; I_X: Intensity of X band; JHD: Joule heat decomposition; LTLM: Linear transmission line method; MCG: Micromechanical cleavage graphene; MLG: Multi-layer graphene; Mo: Molybdenum; SiC: Silicon carbide

Availability of Data and Materials

We declared that materials described in the manuscript, including all relevant raw data, will be freely available to any scientist wishing to use them for non-commercial purposes, without breaching participant confidentiality.

Authors' contributions

ZW conceived the study. ZW and W C coordinated the experiment and participated in the analysis of the data. ZZ worked on the graphene growth. DL carried out the AFM measurements and the analysis of the data. RH carried out the Raman measurements and the analysis of the data. ZZ fabricated the Au-graphene contact. XC and JC did the analysis of the ohmic contact. ZZ and RH wrote the article. All the authors read and approved the manuscript.

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Competing interests

The authors declare that they have no competing interests.

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References

1. Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA (2004) Electric field effect in atomically thin carbon films. Science 306:666–669
2. Geim AK, Novoselov KS (2007) The rise of graphene. Nat Mater 6:183–191
3. Kusdemir E, Özkendir D, Fırat V, Çelebi C (2015) Epitaxial graphene contact electrode for silicon carbide based ultraviolet photodetector. J Phys D Appl Phys 48(9):48095104
4. Chava VSN, Omar SU, Brown G, Shetu SS, Andrews J, Sudarshan TS, Chandrashekhar MVS (2016) Evidence of minority carrier injection efficiency > 90% in an epitaxial graphene/SiC Schottky emitter bipolar junction phototransistor for ultraviolet detection. Appl Phys Lett 108:043502
5. Novoselov KS, Jiang D, Schedin F, Booth TJ, Khotkevich VV, Morozov SV, Geim AK (2005) Two-dimensional atomic crystals. PNAS 102(30):10451–10453
6. Li X, Cai W, An J, Kim S, Nah J, Yang D, Piner R, Velamakanni A, Jung I, Tutuc E, Banerjee SK, Colombo L, Ruoff RS (2009) Large-area synthesis of high-quality and uniform graphene films on copper foils. SCIENCE 324:1312–1314
7. Kim SK, Zhao Y, Jang H, Lee SY, Kim JM, Kim KS, Ahn JH, Kim P, Choi JY, Hong BH (2009) Large-scale pattern growth of graphene films for stretchable transparent electrodes. Nature 457:706–710
8. Tai L, Zhu D, Liu X, Yang T, Wang L, Wang R, Jiang S, Chen Z, Xu Z, Li X (2018) Direct growth of graphene on silicon by metal-free chemical vapor deposition. Nano-Micro Lett 10:20
9. Berger C, Song Z, Li X, Wu X, Brown N, Naud C, Mayou D, Li T, Hass J, Marchenkov AN, Conrad EH, First PN, Heer WA (2006) Electronic confinement and coherence in patterned epitaxial graphene. Science 312:1191–1196
10. Tongay S, Lemaitre M, Fridmann J, Hebard AF, Gila BP, Appleton BR (2012) Drawing graphene nanoribbons on SiC by ion implantation. Appl Phys Lett 100:073501
11. Norimatsu W, Kusunoki M (2014) Epitaxial graphene on SiC{0001}: advances and perspectives. PhysChemChemPhys 16:3501
12. Starke U, Riedl C (2009) Epitaxial graphene on SiC(0001) and SiC(000-1): from surface reconstructions to carbon electronics. J Phys Condens Matter 21:134016
13. Yannopoulos SN, Siokou A, Nasikas KN, Dracopoulos V, Ravani F, Papatheodorou GN (2012) CO_2-laser-induced growth of epitaxial graphene on 6H-SiC(0001). Adv Funct Mater 22:113–120
14. Heer WA, Berger C, Ruan M, Sprinkle M, Li X, Hu Y, Zhang B, Hankinson J, Conrad E (2011) Large area and structured epitaxial graphene produced by confinement controlled sublimation of silicon carbide. PNAS 108:16900–16905
15. Barros EB, Demir NS, Filho AGS, Filho JM, Jorio A, Dresselhaus G, Dresselhaus MS (2005) Raman spectroscopy of graphitic foams. Phys Rev B 71:165422
16. Ni ZH, Chen W, Fan XF, Kuo JL, Yu T, Wee ATS, Shen ZX (2008) Raman spectroscopy of epitaxial graphene on a SiC substrate. Phys Rev B 77:115416
17. Yan J, Zhang Y, Kim P, Pinczuk A (2007) Electric field effect tuning of electron-phonon coupling in graphene. Phys Rev Lett 98:166802
18. Pisana S, Lazzeri M, Casiraghi C, Novoselov KS, Geim AK, Ferrari AC, Mauri F (2007) Breakdown of the adiabatic Born–Oppenheimer approximation in graphene. Nat Mater 6:198–201
19. Casiraghi C, Pisana S, Novoselov KS, Geim AK, Ferrari AC (2007) Raman fingerprint of charged impurities in graphene. Appl Phys Lett 91:233108
20. Hao X, Chen Y, Wang Z, Liu J, Qi F (2014) Morphology and structure of epitaxial graphene grown on 6H–SiC (0001) substrates by modified argon-assisted epitaxial method. Mater Lett 115:144–146
21. Shivaraman S, Chandrashekhar MVS, Boeckl J, Spencer MG (2009) Thickness estimation of epitaxial graphene on SiC using attenuation of substrate Raman intensity. J Electron Mater 38:725–730

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22. Lu W, Boeckl JJ, Mitchel WC (2010) A critical review of growth of low-dimensional carbon nanostructures on SiC (0 0 0 1): impact of growth environment. J Phys D Appl Phys 43:374004

23. Hite JK, Twigg ME, Tedesco JL, Friedman AL, Myers-Ward RL, Eddy CR, Gaskill DK (2011) Epitaxial graphene nucleation on C-face silicon carbide. Nano Lett 11(3):1190–1194

24. Vecchio C, Sonde S, Bongiorno C, Rambach M, Yakimova R, Raineri V, Giannazzo F (2011) Nanoscale structural characterization of epitaxial graphene grown on off-axis 4H-SiC (0001). Nanoscale Res Lett 6:269

25. Kuphal E (1981) Low resistance Ohmic contacts to n- and p-InP. Solid State Electron 24:69–78